Synthesis and Characterization of Conducting Polymer Composite for Electrochemical Sensor Application

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Final-Synopsis

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1. Introduction

The advancements of science and nanotechnology around the world in different areas is remarkable developed but over the past few decades, rapid growth of population density world-wide millions of the peoples are desperately suffering from various diseases like a vitamin deficiency, low blood pressure, internal organs, kidney failure, spinal cord injuries, diabetes, central nervous system of the body and neurological prosthetics, and water contamination, in this regards very much essential to develop a heterostructure electro active sensing material for detection of analytes at low concentration substance.

Currently, sensing nanostructured materials have created curiosity and attracted researcher's interest in this field due to their distinctive physical and chemical properties, mainly their small particle size, wide surface area, biocompatibility, and numerous structural morphologies. But many research groups investigated a variety of nanomaterial's with a lot of research work has been continuing in sensing nanostructured materials with improved surface area, electrical conductivity, sensing the analyte substance, selectivity, sensitivity, low limit of detection, accuracy, and wide linear range, but there are some challenges, and issue are not answer still so far. The biocompatibility advantage is a significant favourable property that may make it desirable to use the nanomaterial as an electrochemical sensor in the medical application for the detection of heavy metals, toxic and non-toxic elements in the human body and environment.

Electro-analytical technique has drawn more attention and curiosity for researcher due to its high accuracy, selectivity, sensitivity, simultaneous detection, detects an analyte species at a low concentration level, high precision, no protocol, and easy operating system with voltammetry techniques [1-3]. Sensors basically composed of a chemical reaction converted into electrical signal modulate to detect the defect or spot related to diseases. Hence, researcher is paid more interest to developing a electrochemical sensor which are highly demands due to detect through blood dynamics in nerve system, and but executing a practical application is a major issue and challenges to use it at different environmental condition and biomolecule analyte species rapid detection with real-time monitoring, accuracy, sensitivity, and selectivity.

Recently, The capability of fabricate the electrochemical sensor using conducting polymers (CPs) such as polyaniline (PANI), polypyrrole (PPY), and polythiophene (PTH) doped with transition metal oxide or sulfide composite such as MoS_2, NiS, Co_3O_4, NiO, SnS, Fe_3O_4, WS_2, CuO, V_2O_5, MoO_3, WO_3, and RuO_2 may advantageous over the noble metals and expand the electrochemical detection of a variety of nanomaterial and different analyte species [4-12]. The electrochemical sensor of nanostructured material has made an appreciable progress in improving the sensitivity and detection of various biomolecule analyte species.

MoS_2 is a desirable electroactive material for electrochemical detection and it has a distinguished physical and chemical properties, strong adsorption behavior, unique-layered structure, adopted a various synthesis methodology, size, and shape of the morphology structure, biocompatibility, convenient for doping and dedoping process, wide electroactive surface area, high electrical and electronic transport properties [13-15]. MoS_2 edges increase the electrocatalytic adsorption activity. In particular, pure MoS_2 nanostructured material

demonstrate the limited electrochemical performance due to poor intrinsic conductivity [16], but when MoS_2 nanostructured material incorporated with any other conducting polymers, which provides the high intrinsic properties in the hybrid composite.

CPs derivative of PANI, and PPY, are 1-D nanostructured materials are considered as a potential candidate in electrochemical sensors, they have consisting of a π conjugate in their backbone, convenient for ease synthesis, reversible doping-dedoping activity, which can be synthesized by various methods and regulate the distinctive surface morphology such as, nanotube, nanofiber and nanosphere [17-22]. These properties are suitable for electrochemical sensor device performance. The nanotube morphology received considerable attention due to their diameter, small thickness; high electrical and chemical stability, resistivity, and fibrul nanotube makes the fast transfer of electron and easily allows the electro-oxidation activity, and high conductivity with a high electrocatalytic and sensing properties.

Co_3O_4 is one of the promising candidates for exposes the sensing properties and it is easily exhibit electrocatalytic behavior with fast detection response of analyte target molecules. The Co_3O_4 is an inherent material with special characteristics, it consists of Co^{2+} tetrahedral hole and Co^{3+} octahedral hole sites with valence spinel crystal structure along with distinctive physical and chemical properties, small size particle, wide surface area, and numerous structural morphologies, various synthesis methods, and biocompatibility. In views of above all, the Co_3O_4 is a favorable application in the biomedical field, detection of heavy metals, toxic and non-toxic elements in the environment.

Copper oxide (CuO) is considered an ideal electroactive material due to CuO is a semi-conducting element with a monoclinic phase structure and unique morphology [23-24], which possessed potential biological properties, high stability, multiple oxidations, and an electronic

state with good reduction ability of oxygen and excellent antimicrobial activity against environmental pathogens which are found in water [25-26]. The use of CPs composite based on the transition metal oxides/sulfides has developed a new pathway for the electrochemical sensors.

In literature review recently, some research group has made significant advancement in nanostructured material for the electrochemical determination of analyte species, it is reported that Hui Mao et al developed a new strategy for electrochemical detection of HQ analyte by using a ternary composite P4VPBA/PPY/GO, which acts as a good sensing material towards the detection of HQ [27]. Tao Yang et al. Synthesized the MoS_2/SPAN by using ultrasonic exfoliation process, the prepared hybrid composite highly negative charged particle, composed a layered structure with wide surface area, the positive charged adenine and guanine analyte detection of electrochemical response which possesses the low limit of detection, good linear range, and improved sensing properties [28]. Shuaihai li et al. illustrated 3D MoS_2-PANI/rGO prepared by hydrothermal route; ternary composite enhanced the electrochemical activity and this material reveals good electrocatalytic activity towards the small molecules and exhibit high sensitivity. J. Samseya et al fabricated a PPY/Au/MEA and used it to detect an Ascorbic acid; the modified PPY/Au/MEA microarray demonstrates the wide linear range, fast response, and high oxidation current response towards the analyte detection of ascorbic acid [29]. Gaopeng et al proposed Co_3O_4/gC_3N_4 GCE studied the hydrazine electrochemical performance in 2M NaOH electrolyte, which shows the good stability, repeatability, and highly selective sensing material for hydrazine sensor [30]. Natesan manjula et al fabricated that the FCO/PPY nanocomposite exhibited an excellent sensitivity, good selectivity, with broad linearity [31].

Therefore, reported literature review provide the evidence for develop the heterostructured material for electrochemical detection for various analyte species with rapid detection, low limit of detection, and high sensitivity. In the present investigation the effort has been made to fabricate the electrochemical sensor of MPN composite, PPYNTs/Co_3O_4, PANI/MoS_2 nanosheets, and PPYNTs/CuO, and examined them to detection sensitive of various analyte species. The dispersion of metal oxide, sulfide on conducting polymer matrix observed results remarkable improved and electrochemical detection demonstrate the low limit of detection, wide linear range and high sensitivity.

2. Motivation for this work

The detection of various analyte species with help of electrochemical sensor has emerged as a most advance device mainly in the medical diagnosis and it is novel device with a simple technique was impetus us to chosen this topic. Therefore, here chosen the transition metal sulfide and metal oxide incorporated with conducting polymer nanofiber nanocomposite and formulated following the aims and objectives of the work.

3. Aims and objective of the present research work

The aims and objectives of the present research work were expressed in the following way,

1. To synthesize a polymer nanofiber and nanotube via chemical method and polymer composite with transition metal oxides, and sulfide prepared by hydrothermal route.
2. To characterized composite by using FTIR spectra, XRD, Raman spectra, EDAX and XPS technique, and surface morphology and elemental mapping images recorded with help of FESEM, and HR-TEM technique.

3. To examine electrochemical properties of composite by using a cyclic voltammetry (CV), difference pulse voltammetry (DPV) and Nyquist plot.
4. To Fabricated electrochemical sensor electrode of various nanostructured materials using drop casting method and to study the electrochemical stability, repeatability, selectivity, sensitivity, linear range and limit of detection, with in order to investigate the fabricated electrode in practical application by using real samples.

4. Outcome of Research work

The proposed research work elaborates the electrochemical sensor for detection of analyte species. The outcome of the research work contributes the comprehensive experimental and theoretical interpretation of device fabrication and working mechanism of electrochemical sensor. The fabricated device demonstrates the wide linear range from 10 μM to 100 μM, sensitivity of 7.19 μA μM cm^{-2} and achieved a low limit of detection (LOD) is 0.40 μM, these results suggested that prepared transition metal sulfide and oxide with conducting polymer composite remarkably favorable in electrochemical sensor applications.

5. Outline of Chapters' distribution in the proposed thesis

The proposed thesis is divided into seven chapters; the first chapter contains the introduction of materials, and their properties as well as conducting polymer nanofiber, nanotubes, and transition metal sulfide, and oxides with their properties. Second chapter deals with the synthesis method and characterization techniques to employ the synthesized conducting polymer with transition metal sulfide and oxide composite and their fabrication process. Third to sixth chapters are working chapters which contain provides the result and discussion

of observed results. The seventh chapter focuses on the summary and scope for the future work.

Chapter I: Introduction

This chapter elaborates the broad information about introduction of the material, electrochemical sensor detection mechanism, conducting polymer nanofiber, nanotube and metal oxide, sulfide composite properties, and analyte species. Literature review for related topic, aim and objective of the work described in details.

Chapter II: Materials, and Experimental Methods

This chapter describes the synthesis methods of conducting polymer nanotube, nanofiber, and transition metal sulfide, and oxides and their characterization to analyze the morphology, structural modification, elemental identification, electrode fabrication and electrochemical parameters.

Chapter III: MoS_2/Polymer nanotube composite material used for electrochemical detection of Dopamine and Ascorbic acid Analytes

This chapter reported on Molybdenum disulphide/polyaniline nanotube (MPN) composite. The 2-D MoS_2 material dispersed on 1-D polyaniline nanocomposite formed the novel 3-D structure morphology, and nanotube morphology structure achieves a greater number of active sites and MoS_2 is a fast ion conductor, which can improve the electrical conductivity, and electrochemical properties. PANI contained a positively occurred nitrogen matrix, it could be explained by the concept of protonation and de-protonation involved in the oxidation process it makes higher sensitivity. The dopamine (DA) and ascorbic acid (AA) are the co-existing compounds in living organism or human body fluid, the DA and AA simultaneous

detection is a difficult and overlapping, but electrochemical sensor resolved this problem. The CV curve indicates quasi reversible redox reaction; and Nyquist plot shows the perfect semi-circle, electrochemical detection of DA and AA exhibit, wide linear range from 5 μM to 6 0μM, and low limit of detection 0.92 μM, 1.42 μM, this composite reveals the synergic effect of electro catalytic oxidation activity towards the detection of DA and AA. Modified MPN GCE electrode material may, helpful in clinical diagnostic applications; MPN composite is one of the fascinating hybrid materials for the evolution or expansion of next-generation electrochemical sensors.

Chapter IV: Study the Electrochemical sensor application based on the Polypyrrole nanotubes /Co_3O_4 nanocomposite for detection of Ascorbic acid

In this chapter, it is explained the micelles self-degraded PPYNTs/Co_3O_4 composite plays a crucial role to detect target analytes such as Ascorbic acid due to cobalt oxide have rich oxidation states Co^{3+}, Co^{2+} and PPYNTs contained nitrogen group an exhibit amine and imine chain. This functional group makes easily adsorb the analyte and provides high oxidation activity. The modified PPYNTs/Co_3O_4 GCE electrochemical detection of Ascorbic acid possesses a wide linear range from 5 μM to 70 μM, low LOD of 0.23 μM, and exhibit high sensitivity of 14.48 μA μM cm^{-2} respectively. The modified PPYNTs/Co_3O_4 GCE electrode material highly favorable for electrochemical detection of Ascorbic acid, and suitable diagnosis tool for medical application.

Chapter V: Study the hydrazine sensor sensitive in the CTAB assisted PANI-MoS_2 nanosheets composite

In this present work, CTAB assisted flower-like PANI-MoS_2 nanosheets. Fabricated PANI-MoS_2 nanosheets GCE electrode CV curve demonstrate quasi-reversible behavior with high

surface area and DPV analysis of hydrazine detection achieved by wide linear range from 10 μM to 100 μM, low limit of detection 0.40 μM, and good sensitivity 7.19 μA μM cm^{-2}. PANI-MoS_2 nanosheets GCE electrode significantly contribute the high electroanalytical oxidation activity due to CTAB surfactant modifies flower like morphology, which makes easily adsorbs the analyte species of hydrazine and exhibit high current rate.

Chapter VI: Study the detection of hydroquinone sensitivity in Polypyrrole nanotube/Copper oxide nanocomposite

This chapter elaborates the electrochemical detection of hydroquinone analyte molecule through sensing material Polypyyrole/Copper oxide (PNTs/CuO) nano composite. PNTs/CuO composite UV-absorption spectra possessed wavelength of 269 nm and 469 nm. FTIR spectra reveals the presence of CuO band at 660 cm^{-1}, FESEM images confirms the nanotube morphology and CuO homogeneously dispersed on the surface of PNTs. The CV curve demonstrated that the excellent oxidation and reduction behavior with wide surface area and DPV analysis of PNTs/CuO possessed a high electrocatalytic oxidation activity towards the hydroquinone analyte detection.

Chapter VII: Conclusions and Scope for future work

This chapter summarizes the present results and outline of the future work and opportunity in this field.

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